# Electrochemical Studies of Some Selected Aliphatic and Aromatic Ketoximes

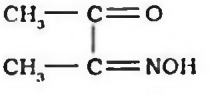
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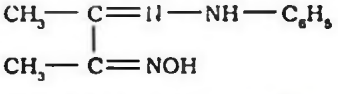
Diacetylmonoxime, diacetylmonoxime phenylhydrazone, benzilmonoxime and benzildioxime have been studied electrochemically using DC, AC and differential pulse polarography over a wide pH range of 2.0 to 12.0. Millicoulometry was employed for the determination of the number of electrons. Based on these results, kinetic parameters such as diffusion coefficients (D) and heterogeneous forward rate constants ($k^{\circ}_{fh}$) are evaluated and reported. The reduction mechanism is proposed. An analytical procedure has been standardised for the estimation of the four compounds.

Polarographic behaviour of certain α - ketoximes was studied by several investigators [1-5]. The study was restricted to certain acid/alkaline pH range or attention was limited to a comparison of reduction potentials. The investigators were not always in complete agreement on the mechanisms of the reactions. The mechanistic aspects can be discussed more definitively by utilising modern electrochemical techniques to the cathodic reduction of these ketoximes.

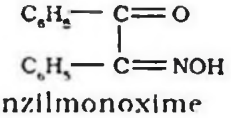
It is of interest to study the electrochemical behaviour of oxime group in the vicinity of both electron-donating and electron withdrawing groups. In compounds A and B, the oxime group and azomethine group are planked by two electron releasing (+I) methyl groups. In compound C and D, electron withdrawing (-I) phenyl groups are present.



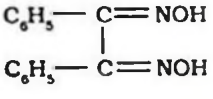
A. Diacetylmonoxime



B. Diacetylmonoxime phenylhydrazone



C. Benzilmonoxime



D. Benzildioxime

These compounds are used as analytical reagents and as drug formulations; So differential pulse polarographic technique is employed for working out analytical procedures for the estimation of these systems.



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## EXPERIMENTAL

### Apparatus

Model 364 polarographic analyser supplied from PARC coupled with BD8 Kipp and Zonen x-t recorder was used for DC polarographic measurements. Other techniques were carried out using a Metrohm E 506 polarecord coupled with E612 VA-Scanner, E 648 VA-combistand, E608 VA-controller and digital electronics 2000 x-y/t recorder. All electrochemical measurements were carried out at 25 ±1°C using a conventional three electrode design. The DME (area 0.2223 $cm^2$) and HMDE (area 0.032 $cm^2$) were used as working electrodes. Ag/AgCl(s), $Cl^-$ electrode was the reference for cyclic voltammetry, AC polarography and differential pulse polarography; saturated calomel electrode (SCE) was the refernce in DC polarography. Platinum electrode was used as counter electrode in all cases. A modified cell with mercury pool cathode, SCE, platinum wire gauze electrode and a spot galvanometer were used for controlled potential electrolysis.

### Material

Diacetylmonoxime and benzildioxime samples were procured from Loba Chemicals, Bombay. Benzil monoxime (C) and phenlhydrozone (B) were prepared by methods described in literature [6]

5.0 gm of hydroxylamine hydrochloride was dissolved in 20 ml of water, 20 ml of 10% sodium hydroxide solution and 2.0 gm of the corresponding ketone was added to this. Sufficient ethanol was added to the mixture to give a clear solution. The mixture was refluxed for 10-15 minutes or warmed on a water bath for 10-15 minutes and then cooled. The crystalline product was filtered off and recrystallised from dilute ethanol.

Universal buffers of pH 2.0 to 12.0 were prepared by using 0.2 M boric acid, 0.05 M citric acid and 0.1 M trisodium orthophosphate. All chemicals used were of pure analar grade. Stock solution was prepared by dissolving the required amount of electroactive species in triple distilled water and making up with the supporting electrolyte to obtain the desired concentration. The test solution was purged with purified nitrogen gas for 10 minutes before the voltammograms were taken.

## RESULTS AND DISCUSSION

Diacetylmonoxime gave a single well defined cathodic wave/peak (fig.1) in all the buffer systems studied over the entire pH range (2.0 to 12.0). The step correponded to four electron reduction (oxime reduction). In case of diacetylmonoxime phenylhydrazone, two well separated waves/peaks of equal heights were observed in acidic range of pH up to 6.0 (Fig.2) whereas in basic media (pH > 8.0) no reduction was observed. Each of the steps corresponded to four electrons reduction.

Benzilmonoxime gave single well defined

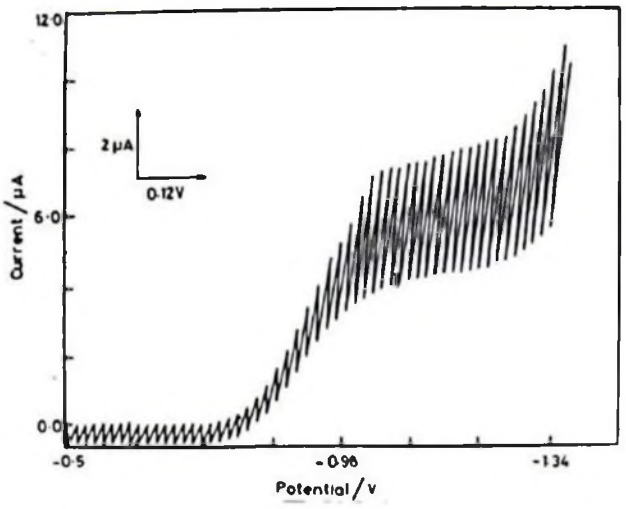



**Fig 1. Typical DC Polarogram of Diacetylmonoxime**
pH 4.0; Concentration 0.5 mM;
Drop time 3 sec

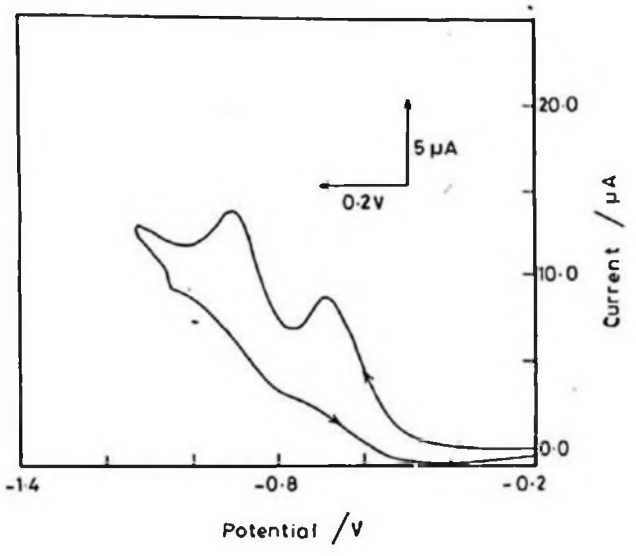



**Fig 2. Typical Cyclic Voltammogram of Diacetylmonoxime phenylhydrazone**
0.1 M $HClO_4$ medium;
Concentration 0.5 mM;
Scan rate $40mVs^{-1}$

four electron reduction wave/peak in all the techniques employed (the reduction of oxime group) in the entire pH range (in 0.1 M $HClO_4$ and solutions of pH 2.0 to 12.0). Typical voltammogram is shown

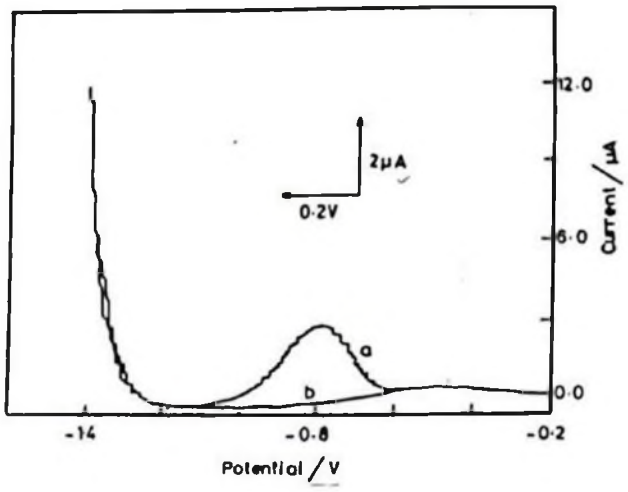



**Fig 3. Typical AC Polarogram of Benzilmonoxime**
pH 6.0; Concentration 0.5 mM;
Drop time 3 sec

in Fig.3. A well defined single wave/ peak observed for benzildioxime in the acidic media (2.0 < pH < 8.0) is ascribed to the reduction of dioxime group to the diamino product in an eight electron step. Typical voltammogram is shown in Fig.4. In alkaline solutions (pH > 8.0), no reduction was observed.

Diffusion current and peak current variations were found to be perfectly linear with square root of mercury column height (DC), scan rate (CV) and also square root of rotational velocities (Rotating Ring Disc Voltammetry) indicating that the electrode process is diffusion controlled. The collection efficiencies (N) calculated from rotating ring disk voltammetry [0.174 for diacetylmanoxime at pH 4.0; 0.172 for diacetylmonoxime phenylhydrazone at pH 4.0; 0.171 for benzilmonoxime at pH 2.0 and 0.176 for benzildioxime in 0.1 M $HClO_4$] are seen to be in good agreement

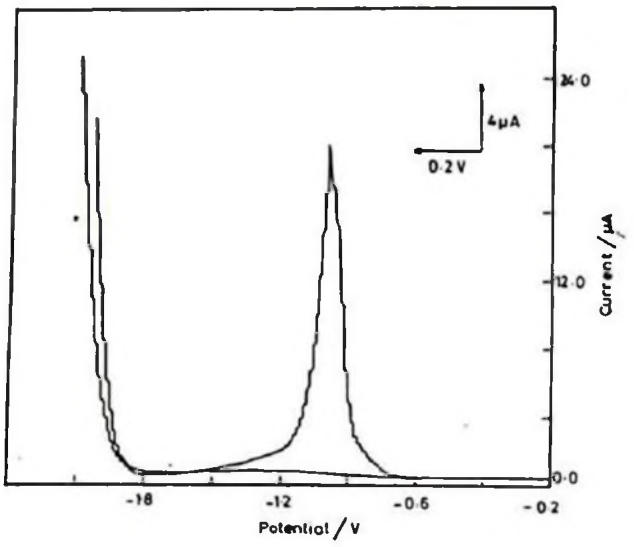



**Fig. 4. Typical Differential Pulse Polarogram of Benzildioxime**
pH 6.0; Concentration 0.5 mM; Drop time 2 sec.

with the theoretical value (0.179). This also indicates the diffusion controlled nature of the electrode reaction.

But it was irreversible in nature as seen from the disobedience ot Tomes' criterion, log plot analysis and dependence of $E_{1/2}$ with concentration of electroactive species in DC polarography; it was also seen by the absence of anodic peak in the reverse scan and variation of peak potential with the scan rate in cyclic votammetry. The marginal variation of peak potential ($E_m$) with concentration and non-linearity in the plot of $i_m$ *vs* $(1 - \sigma)/(1 + \sigma)$ in differential pulse polarography and low currents observed in AC polarography also confirm the irreversible nature of the electrode process.

The results of millicoulometry showed the number of electrons to be eight in the case of benzildioxime and four in all other cases. This was attributed to oxime group reduction. Controlled potential electrolysis experiments were carried out for (1) diacetylmonoxime in pH 2 at -0.9 V , (2) diacetylmonoxime phenylhydrozone in 0.1 M $HClO_4$ at -1.0V, (3) benzilmonoxime in solution of pH 2.0 at -0.75 V and (4) benzildioxime also at pH 2.0 at -0.85 V. The product was shown to be the corresponding amine in every case (I.R. spectral studies in Nujol medium). The four electron reduction in every case is due to the reduction of oxime to the corresponding amine. The eight electron reduction of benzildioxime is due to the reduction of two oxime groups to two amine groups. In case of diacetylmonoxime phenylhydrazone (compound B) the two steps are due to reduction of oxime to amine and phenylhydrazone to the corresponding amine. Oxime group is reduced more easily (because of the presence of polarity in the N-O bond) than the phenyl hydrazone group.

The kinetic parameters such as diffusion coefficients and heterogeneous forward rate constant ($k_h^*$) were calculated using data from different techniques and at different pH values (Table 1-4).

## Table 1

**Typical Kinetic Data of Diacetylmonoxime**

T = 25 ±1°C; Area of DME 0.2223 $cm^2$; Area of HMDE 0.032 $cm^2$
Potentials in Volts; D in $cm^2s^{-1}$; Rate constant in $cms^{-1}$

| | 0.1 M Acid | pH 2.0 | pH 4.0 | pH 6.0 | pH 8.0 | pH 10.0 | pH 12.0 |
|---|---|---|---|---|---|---|---|
| **DC Polarography** | | | | | | | |
| $E_{1/2}$ | 0.72 | 0.87 | 0.90 | 0.98 | 1.04 | 1.13 | 1.22 |
| $Dx10^5$ | 7.43 | 7.01 | 6.43 | 5.94 | 5.90 | 5.62 | 5.08 |
| $k^{\circ}_{f,h}$ | $7.34x10^{-8}$ | $1.38x10^{-9}$ | $4.82x10^{-12}$ | $8.55x10^{-12}$ | $1.44x10^{-13}$ | $5.35x10^{-15}$ | $2.10x10^{-17}$ |
| **Cyclic voltammetry** | | | | | | | |
| $E_p$ | 0.71 | 0.82 | 0.89 | 0.97 | 1.08 | 1.17 | 1.20 |
| $Dx10^5$ | 7.21 | 6.93 | 6.45 | 5.91 | 5.67 | 5.15 | 5.13 |
| $k^{\circ}_{f,h}$ | $6.37x10^{-8}$ | $1.92x10^{-8}$ | $4.91x10^{-11}$ | $2.78x10^{-13}$ | $3.04x10^{-14}$ | $4.55x10^{-15}$ | $7.53x10^{-17}$ |
| **AC Polarography** | | | | | | | |
| $E_a$ | 0.70 | 0.81 | 0.88 | 0.95 | 1.03 | 1.13 | 1.21 |
| $Dx10^5$ | 6.99 | 6.87 | 6.01 | 5.88 | 5.72 | 5.13 | 5.01 |
| $k_a$ | $2.24x10^{-5}$ | $8.73x10^{-6}$ | $2.79x10^{-6}$ | $1.53x10^{-8}$ | $8.76x10^{-10}$ | $2.64x10^{-11}$ | $6.77x10^{-13}$ |
| **DPP** | | | | | | | |
| $E_m$ | 0.69 | 0.78 | 0.86 | 0.93 | 1.00 | 1.12 | 1.19 |
| Dx105 | 7.11 | 6.93 | 6.84 | 5.63 | 5.48 | 5.32 | 5.10 |
| $k^{\circ}_{f,h}$ | $9.87x10^{-8}$ | $3.13x10^{-8}$ | $4.88x10^{-11}$ | $1.67x10^{-12}$ | $7.39x10^{-14}$ | $9.12x10^{-15}$ | $5.49x10^{-10}$ |
| **Rotating ring disc voltammetry** | | | | | | | |
| $Dx10^5$ | 8.28 | 8.19 | 7.66 | 6.45 | 6.37 | 6.28 | 6.15 |
| $k^{\circ}_{f,h}$ | $9.67x10^{-7}$ | $1.32x10^{-7}$ | $2.66x10^{-9}$ | $3.32x10^{-10}$ | $4.78x10^{-12}$ | $2.83x10^{-13}$ | $8.12x10^{-15}$ |

The diffusion coefficient values evaluated from all the techniques are in good agreement. No adsorption complications appear to be present in any electrode process. As expected, diffusion coefficient values slightly decreased with increase in the molecular weight of the electroactive species. In all cases diffusion coefficient slightly decreased with increase in pH and this may be attributed to the decrease in the availability of protons with increase in pH.

In general, rate constant values are observed to be high in acidic medium. The rate of reaction is fast in this medium since protonated form [ ( >C = NOH)$H^+$] gets reduced. The rate decreases with increase in pH. This trend shows that

## Table 2

**Typical kinetic data of diacetylmonoxime phenylhdrazone**

T = 25 ±1°C; Area of DME 0.2223 $cm^2$; Area of HMDE 0.032 $cm^2$
Potentials in Volts; D in $cm^2s^{-1}$; Rate constant in $cms^{-1}$

| | $HClO_4$ 0.1 M | | pH= 2.0 | | pH= 4.0 | | pH= 6.0 | |
|---|---|---|---|---|---|---|---|---|
| | I | II | I | II | I | II | I | II |
| **DC Polarography** | | | | | | | | |
| $E_{1/2}$ | 0.73 | 0.92 | 0.82 | 1.00 | 0.92 | 1.12 | 1.07 | - |
| $Dx10^5$ | 7.35 | 7.10 | 7.13 | 6.03 | 6.85 | 5.25 | 6.32 | - |
| $k^\circ_{f,h}$ | $5.8110^{-9}$ | $5.10x10^{-11}$ | $3.11x10^{-10}$ | $2.52x10^{-13}$ | $2.74x10^{-12}$ | $8.64x10^{-15}$ | $4.63x10^{-14}$ | - |
| **Cyclic voltammetry** | | | | | | | | |
| $E_p$ | 0.71 | 0.90 | 0.84 | 1.04 | 0.98 | 1.18 | 1.12 | - |
| $Dx10^5$ | 7.16 | 6.95 | 7.05 | 6.15 | 6.61 | 5.34 | 6.25 | - |
| $k^\circ_{f,h}$ | $7.44x10^{-9}$ | $5.26x10^{-11}$ | $4.87x10^{-11}$ | $4.03x10^{-13}$ | $2.66x10^{-10}$ | $3.32x10^{-14}$ | $6.11x10^{-14}$ | - |
| **AC Polarography** | | | | | | | | |
| $E_\phi$ | 0.69 | 0.83 | 0.81 | 0.99 | 0.95 | 1.14 | 1.10 | 1.25 |
| $Dx10^5$ | 7.02 | 6.86 | 6.99 | 6.11 | 6.15 | 5.93 | 6.03 | 4.49 |
| $k^\circ_{f,h}$ | $9.61x10^{-5}$ | $1.01x10^{-5}$ | $3.73x10^{-6}$ | $2.39x10^{-7}$ | $8.93x10^{-8}$ | $4.45x10^{-11}$ | $3.15x10^{-9}$ | $1.13x10^{-18}$ |
| **DPP** | | | | | | | | |
| $\Sigma_m$ | 0.72 | 0.91 | 0.82 | 1.03 | 0.94 | 1.12 | 1.10 | |
| $Dx10^5$ | 6.99 | 6.74 | 6.48 | 6.02 | 5.81 | 5.07 | 4.95 | |
| $k^\circ_{f,h}$ | $7.73x10^{-9}$ | $1.47x10^{-11}$ | $9.47x10^{-10}$ | $1.99x10^{-12}$ | $1.77x10^{-12}$ | $6.86x10^{-14}$ | $8.43x10^{-15}$ | |
| **Rotating ring dise voltammetry** | | | | | | | | |
| $Dx10^5$ | 8.22 | 8.15 | 8.19 | 8.01 | 7.45 | 7.21 | 7.32 | |
| $k^\circ_{f,h}$ | $9.61x10^{-7}$ | $8.01x10^{-9}$ | $3.73x10^{-9}$ | $6.11x10^{-10}$ | $1.24x10^{-11}$ | $5.37x10^{-13}$ | $4.68x10^{-13}$ | |

the electrode process tends to become more and more irreversible with increase in pH of the solution. The AC polarographic rate constant values are found to be different from the values obtained from other techniques since these relate to standard potential. The rate constant values obtained from all the techniques show that the reduction is more difficult in the case of diacetylmonoxime phenylhydrazone. From comparison of $E_{1/2}$ values, the ease of reduction is noticed to be in the order Benzil monoxime > Benzil dioxime > Diacetylmonoxime > diacetyl monoxime phenylhydrazone.

The species getting reduced in acidic

## Table 3

**Typical Kinetic Data of Benzilmonoxime**

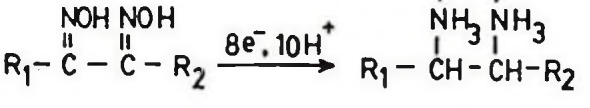
T = 25 ±1°C; Area of DME 0.2223 $cm^2$; Area of HMDE 0.032 $cm^2$
Potentials in Volts; D in $cm^2sec^{-1}$; Rate constant in $cm^{-1}$

| | $HClO_4$ 0.1M | pH=2.0 | pH=4.0 | pH=6.0 | pH=8.0 | pH=10.0 | pH=12.0 |
|---|---|---|---|---|---|---|---|
| **DCP** | | | | | | | |
| $E_{1/2}$ | 0.51 | 0.62 | 0.69 | 0.75 | 0.89 | 0.94 | 1.02 |
| $Dx10_5$ | 6.45 | 6.11 | 5.73 | 5.28 | 4.23 | 5.13 | 5.11 |
| $k^*_{f,h}$ | $4.37x10^{-6}$ | $6.43x10^{-8}$ | $1.83x10^{-9}$ | $3.11x10^{-11}$ | $3.42x10^{-12}$ | $2.33x10^{-14}$ | $6.93x10^{-15}$ |
| **Cyclic voltammetry** | | | | | | | |
| $E_p$ | 0.55 | 0.62 | 0.70 | 0.76 | 0.85 | 0.92 | 0.99 |
| $Dx10^5$ | 6.22 | 6.19 | 5.43 | 5.09 | 4.98 | 4.93 | 5.01 |
| $k^*_{f,h}$ | $3.41x10^{-6}$ | $9.09x10^{-7}$ | $5.19x10^{-9}$ | $3.52x10^{-11}$ | $2.4\ x10^{-12}$ | $6.42x10^{-13}$ | $2.20x10^{-15}$ |
| **ACP** | | | | | | | |
| $E_a$ | 0.54 | 0.60 | 0.66 | 0.74 | 0.86 | 0.93 | 1.01 |
| $Dx10^5$ | 6.12 | 5.64 | 5.21 | 5.08 | 5.01 | 4.90 | 4.76 |
| $k_a$ | $7.33x10^{-3}$ | $4.87x10^{-3}$ | $2.56x10^{-5}$ | $6.02x10^{-6}$ | $4.03x10^{-8}$ | $2.66x10^{-10}$ | $3.32x10^{-12}$ |
| **DPP** | | | | | | | |
| $E_m$ | 0.52 | 0.60 | 0.66 | 0.74 | 0.82 | 0.94 | 1.05 |
| $Dx10^5$ | 6.08 | 5.75 | 5.05 | 4.99 | 4.85 | 4.73 | 4.68 |
| $k^*_{f,h}$ | $1.37x10^{-5}$ | $8.99x10^{-7}$ | $2.19x10^{-9}$ | $6.19x10^{-10}$ | $5.38x10^{-11}$ | $1.59x10^{-13}$ | $4.08x10^{-15}$ |
| **Rotating Ring Disc Voltammetry** | | | | | | | |
| $Dx10^5$ | 7.56 | 6.78 | 6.43 | 6.28 | 6.19 | 6.03 | 5.98 |
| $k^*_{f,h}$ | $1.24x10^{-5}$ | $8.73x10^{-6}$ | $3.93x10^{-8}$ | $4.45x10^{-9}$ | $5.37x10^{-11}$ | $3.88x10^{-13}$ | $9.57x10^{-14}$ |

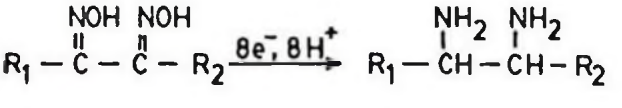
media is the protonated oxime species, the neutral oxime species in neutral medium. In alkaline medium oxime exists as the conjugate base = NO-. Based on the results obtained, the electrochmeical reduction behaviour of the for oximes are proposed as follows:

benzil dioxime $R_1 : R_2 : -C_6H_5$

In acidic media ( $pH \leq 4.0$)



In neutral media ( $6.0 \leq pH \leq 8.0$ )



## Table 4

**Typical Kinetic Data of Benzildioxime**

T = 25 ±1°C; Area of DME 0.2223 $cm^2$; Area of HMDE 0.032 $cm^2$
Potentials in Volts; D in $cm^2sec^{-1}$; Rate constant in $cm^{-1}$

| | $HClO_4$ 0.1M | pH= 2.0 | 4.0 | 6.0 | 8.0 |
|---|---|---|---|---|---|
| **DCPolarography** | | | | | |
| $E_{1/2}$ | 0.62 | 0.74 | 0.81 | 0.88 | 0.95 |
| $Dx10^5$ | 6.25 | 6.05 | 5.23 | 5.08 | 4.90 |
| $k^{\circ}_{f,h}$ $cms^{-1}$ | $3.16x10^{-7}$ | $4.88x10^{-8}$ | $5.49x10^{-10}$ | $2.12x10^{-12}$ | $5.44x10^{-14}$ |
| **Cyclic voltammetry** | | | | | |
| $E_p$ | 0.63 | 0.74 | 0.80 | 0.87 | 0.94 |
| Dx105 | 6.01 | 5.90 | 5.15 | 5.05 | 5.02 |
| $k_{f,h}$ $cms^{-1}$ | $7.39x10^{-7}$ | $5.45x10^{-9}$ | $1.78x10^{-9}$ | $3.52x10^{-12}$ | $2.41x10^{-14}$ |
| **ACPolarography** | | | | | |
| $E_a$ | 0.63 | 0.72 | 0.80 | 0.87 | 0.94 |
| $Dx10^5$ | 5.99 | 5.15 | 4.93 | 4.49 | 4.23 |
| $k_a$ $cms^{-1}$ | $2.40x10^{-4}$ | $1.11x10^{-4}$ | $2.45x10^{-5}$ | $3.15x10^{-7}$ | $4.13x10^{-9}$ |
| **DPP** | | | | | |
| $E_m$ | 0.61 | 0.72 | 0.82 | 0.86 | 0.93 |
| Dx105 | 5.92 | 5.23 | 5.19 | 5.03 | 4.89 |
| $kf_{,h}$ $cms^{-1}$ | $3.24x10^{-7}$ | $5.59x10^{-9}$ | $8.34x10^{-10}$ | $2.3x10^{-20}$ | $4.97x10^{-13}$ |
| **Rotating ring disc voltammetry** | | | | | |
| $Dx10^5$ | 7.23 | 6.42 | 6.25 | 5.98 | 5.47 |
| $k^{\circ}_{f,h}$ $cms^{-1}$ | $1.37x10^{-5}$ | $8.99x10^{-6}$ | $2.19x10^{-8}$ | $5.38x10^{-10}$ | $4.08x10^{-12}$ |

## Analysis

The polarographic wave obtained in acidic media is well resolved and can be used for analysis. In the present study, the experimental data of differential pulse polarography are used to work out analytical procedures for the estimation of the title compounds. Modulation amplitude of 50 mV and drop time of 2 sec was found suitable for analytical work. The peak height is found to be linear over a range of 2 orders. The lower detection limits are in the range $10^{-7}$ M (Table 5).

The procedure for standard addition method is as follows: Stock solution ($1.0x10^{-5}$ M) is prepared by dissolving the appropriate amount of the

electroactive species in triple distilled water. 1 ml of standard solution is transferred into a polarographic cell and made up with 9 ml of the supporting electrolyte and then deoxygenated with nitrogen gas for 10 minutes. After recording the polarogram, small increments (0.2 ml) of standard solution are added and the polarograms are recorded after each addition under similar conditions. The relative standard deviation (S.D) and correlation coefficient (C Coef.) for 10 replicants are as shown in Table 5. Lower detection limit (D.L) was of the order $10^{-7}$ M

Table 5

**Analysis of oximes by DPP using Standard addition method**

| oxime | Linear range | D.Lx$10^{7}$ | S.D % | C Coef. |
|---|---|---|---|---|
| A Diacetyl | $10x10^{-5}x3.3x10^{-7}$ | 2.9 | 1.3 | 0.979 |
| B Phenyl | $1x10^{-5}$-$3.45x10^{-7}$ | 3.1 | 2.1 | 0.993 |
| C Benzil mon | $1x10^{-5}$-$2.1x10^{-7}$ | 1.85 | 1.4 | 0.991 |
| D Benzil di | $1.5x10^{-5}$-$1.9x10^{-7}$ | 1.75 | 1.29 | 0.998 |

Diacetylmonoxime is successfully determined in a pharamceutical (injection) formulation without any prior separation by using the recommended analytical procedure. The assay results are given in Table 6.

## Table 6

**Assay of diacetylmonoxime dosage form by DPP**

Labelled amount of diacetyl monoxime injection used 10mg

| Supporting electrolyte | Amount found/mg | Recovery (%) | Standard deviation |
|---|---|---|---|
| 0.1M $HClO_4$ | 9.98 | 99.80 | 0.019 |
| pH 2.0 | 9.91 | 99.20 | 0.024 |

## ACKNOWLEDGEMENTS

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